

In the Claims

1. (currently amended) A formulation comprising at least one granulate containing
 - a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,
 - b) from 10 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,
 - c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,
 - d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
 - e) from 3 to 15 % by weight water, based on the total weight of the granulate;

where the phthalocyanine compound is of formula (1a)



wherein

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z₁; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;

q is 0, 1 or 2;

r is from 1 to 4;

Q₁ is a sulfo or carboxy group; or is a radical of formula

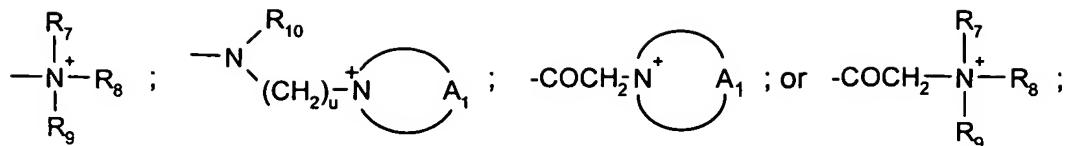
-SO₂X₂-R₆-X₃⁺; -O-R₆-X₃⁺; or -(CH₂)_t-Y₁⁺;

wherein

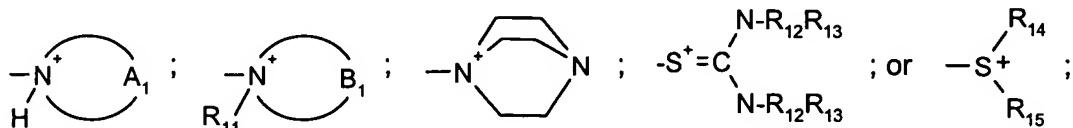
R₆ is branched or unbranched C₁-C₈alkylene; or 1,3- or 1,4-phenylene;

X₂ is -NH-; or -N-C₁-C₅alkyl-;

X₃⁺ is a group of formula



and, in the case where $R_6 = C_1-C_8$ alkylene, may also be a group of formula



Y_1^+ is a group of formula $\begin{array}{c} -N^+ \\ | \\ H \end{array} \text{---} A_1$; or $\begin{array}{c} R_{14} \\ | \\ -S^+ \\ | \\ R_{15} \end{array}$; or $\begin{array}{c} N-R_{12}R_{13} \\ | \\ + \\ -S=C \\ | \\ N-R_{12}R_{13} \end{array}$;

t is 0 or 1;

in which above formulae.

R₇ and R₈ are each independently of the other C₁-C₆alkyl;

R₉ is C₁-C₆alkyl; C₅-C₇cycloalkyl; or NR₁₁R₁₂;

R_{10} and R_{11} are each independently of the other C₁-C₅alkyl;

R_{12} and R_{13} are each independently of the other hydrogen or C_1-C_5 alkyl;

R_{14} and R_{15} are each independently of the other unsubstituted or hydroxy-, cyano-, carboxy-, C_1 - C_6 alkoxy-carbonyl-, C_1 - C_6 alkoxy-, phenyl-, naphthyl- or pyridyl-substituted C_1 - C_6 alkyl;

u is from 1 to 6;

A₁ is the balance of an aromatic 5- to 7-membered nitrogen heterocycle which may contain one or two further nitrogen atoms as ring members, and

B₁ is the balance of a saturated 5- to 7-membered nitrogen heterocycle which may contain 1 or 2 further nitrogen, oxygen and/or sulfur atoms as ring members:

A⁻ is an organic or inorganic anion

and

s in the case of monovalent anions A^- is equal to r and in the case of polyvalent anions is $\leq r$, it being necessary for A_s^- to balance the positive charge; and when $r \neq 1$, the radicals Q_1 may be identical or different.

and wherein the phthalocyanine ring system may also contain further solubility-imparting groups.

and

where the inorganic salts are selected from the group consisting of alkali metal salts of carbonates, hydrogen carbonates, phosphates, polyphosphates, sulfates, silicates, halides and pyrophosphates,

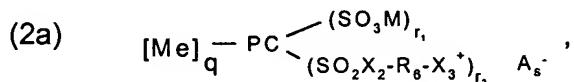
and

where the low-molecular-weight organic acids or and salts thereof is are selected from the group consisting of oxalic acid, tartaric acid, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluenesulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid, and/or polyacrylic acid and/or a salts thereof.

2. (original) A formulation according to claim 1, wherein the granulate comprises, as phthalocyanine compound, at least one water-soluble Zn(II), Fe(II), Ca(II), Mg(II), Na(I), K(I), Al, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III), Zr(IV), In(III), Sn(IV) or Hf(VI) phthalocyanine compound.

3. (canceled)

4. (previously presented) A formulation according to claim 1, wherein the granulate comprises at least one phthalocyanine compound of formula



wherein

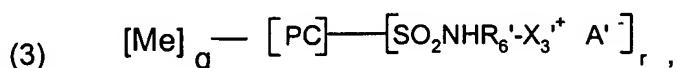
Me, q, PC, X₂, X₃ and R₆ are as defined for formula (1a),

M is hydrogen; or an alkali metal ion, ammonium ion or amine salt ion;

and the sum of the numbers r₁ and r₂ is from 1 to 4, and

A_s⁻ exactly balances the positive charge of the remainder of the molecule,

or of formula

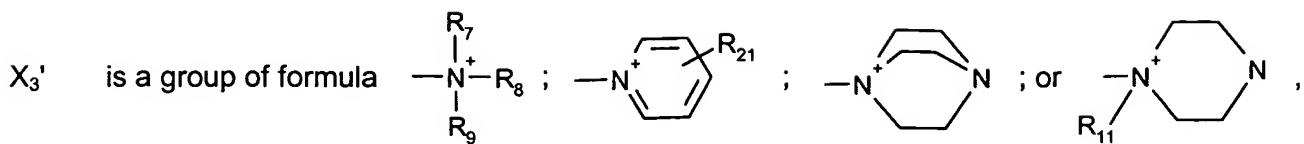


wherein

Me, q and PC are as defined for formula (1a),

R_{6'} is C₂-C₆alkylene;

r is a number from 1 to 4;



wherein

R₇ and R₈ are each independently of the other unsubstituted or hydroxy-, cyano-, halo- or phenyl-substituted C₁-C₄alkyl;

R₉ is R₇; cyclohexyl or amino;

R₁₁ is C₁-C₄alkyl;

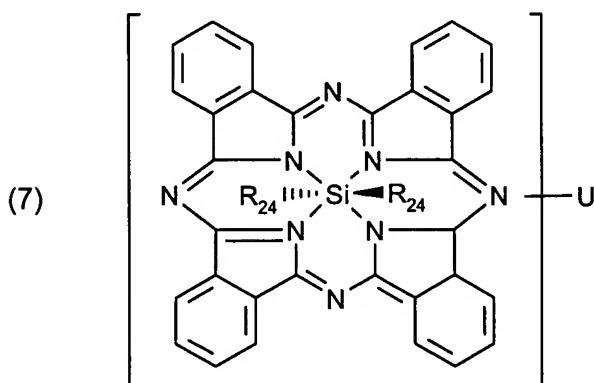
R₂₁ is C₁-C₄alkyl; C₁-C₄alkoxy; halogen; carboxy; C₁-C₄alkoxy-carbonyl or hydroxy; and

A' is a halide ion, alkylsulfate ion or arylsulfate ion;

it being possible for the radicals -SO₂NHR'₆-X_{3'}A' to be identical or different.

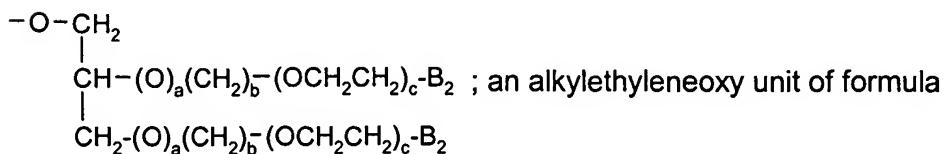
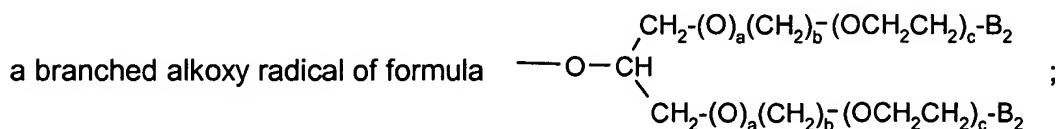
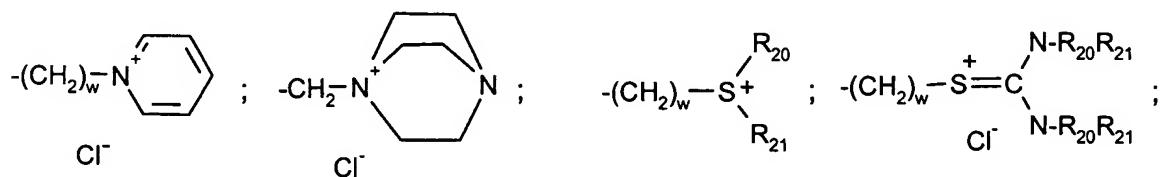
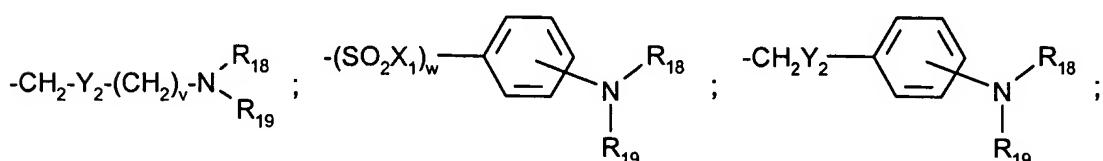
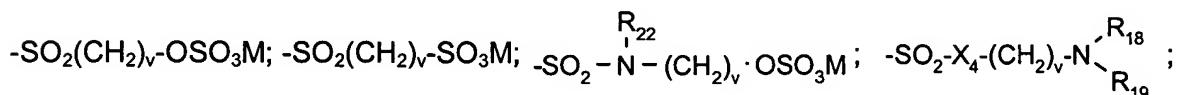
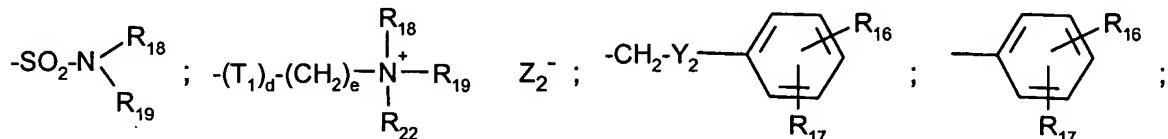
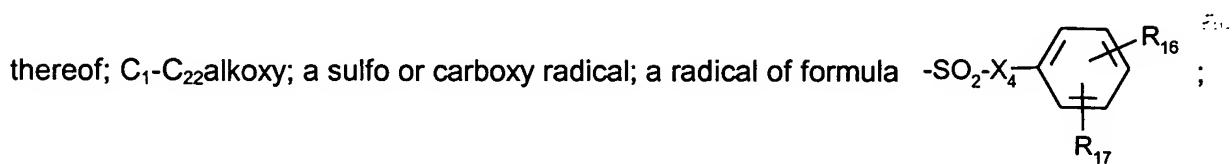
5-8. (canceled)

9. (currently amended) A formulation according to claim 1, wherein the granulate comprises at least one phthalocyanine compound of formula



wherein

R_{24} is hydroxy; C_1 - C_{22} alkyl; branched C_4 - C_{22} alkyl; C_1 - C_{22} alkenyl; branched C_4 - C_{22} alkenyl or a mixture



$-(T_1)_d-(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_a-\text{B}_3$ or an ester of formula COOR_{23} ; and

U is $[\text{Q}_1]_r^+\text{A}_s^-$; $[[\text{Q}_2]]$

$R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, B_2, B_3, M, Q_1, [[\text{Q}_2]] A_s, T_1, X_1, X_4, Y_2, Z_2^-$, a, b, c, d, e, r, v and w therein being as defined for formulae (1a) and (1b).

10-13. (canceled)

14. (previously presented) A formulation according to claim 1, wherein the granulate comprises, as anionic dispersing agent, one or more condensation products selected from the group consisting of: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated biphenyls or biphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkyl naphthalenesulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalenemethanesulfonates, ligno- or oxyligno-sulfonates and heterocyclic polysulfonic acids.

15. (canceled)

16. (previously presented) A formulation according to claim 1, wherein the granulate comprises, as water-soluble (but not necessarily film-forming) polymer, one or more compounds selected from the group consisting of: gelatins, polyacrylates, polymethacrylates, copolymers of ethyl acrylate, methyl methacrylate and methacrylic acid (ammonium salt), polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, copolymers of vinylpyrrolidone with long-chain olefins, poly(vinyl-pyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of inylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethyl cellulose, hydroxymethyl cellulose, polyvinyl alcohols, hydrolysed and non-hydrolysed polyvinyl acetate, copolymers of maleic acid with unsaturated hydrocarbons and also mixed polymerisation products of the mentioned polymers, polyethylene glycol (MW = 4000 – 20 000), copolymers of ethylene oxide with propylene oxide (MW > 3500), condensation products (block polymerisation products) of alkylene oxides, copolymers of

vinylpyrrolidone with vinyl acetate, ethylene oxide-propylene oxide addition products with diamines, polystyrenesulfonic acid, polyethylenesulfonic acid, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropyl methylcellulose, sodium carboxymethyl cellulose, hydroxypropyl methylcellulose phthalate, maltodextrin, starch, sucrose, lactose, enzymatically modified and subsequently hydrated sugars, polyaspartic acid and tragacanth.

17-23. (canceled)

24. (previously presented) A formulation according to claim 1, wherein the granulate further comprises from 0 to 5 % by weight of a wetting agent, a disintegrant, a filler, a water-insoluble or water-soluble dye or pigment, and/or a dissolution accelerator, an optical brightener, a zeolite, talc, powdered cellulose, fibrous cellulose, microcrystalline cellulose, kaolin, TiO₂, SiO₂ and/or magnesium trisilicate.

25. (previously presented) A formulation according to claim 1, wherein the granulate consists of

- a) from 4 to 30 % by weight of at least one water-soluble phthalocyanine compound,
- b) from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer,
- c) from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof,
- d) from 0 to 5 % by weight at least one further additive, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

26-27. (canceled)

28. (previously presented) A formulation according to claim 1, wherein the granulate has an average particle size of < 500 µm.

29. (canceled)

30. (previously presented) A washing agent composition, washing agent additive or additive concentrate which comprises a formulation according to claim 1.

31. (previously presented) A composition according to claim 30, which is a component of a pre- and/or after-treatment agent, stain-removing salt, washing-power enhancer, fabric conditioner, bleaching agent and/or UV-protection enhancer.

32. (canceled)

33. (previously presented) A washing agent formulation consisting of

- I) from 5 to 70 % A) of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,
- II) from 5 to 60 % C) of at least one builder substance, based on the total weight of the washing agent formulation,
- III) from 0 to 30 % D) of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent formulation, and
- IV) from 0.001 to 1 % E) of at least one granulate as defined in claim 1, and
- V) from 0 to 60 % F) of at least one further additive, and
- VI) from 0 to 5 % G) water.

34. (canceled)

35. (previously presented) A process for the preparation of a granulate according to claim 1, wherein firstly an aqueous solution of the phthalocyanine compound is prepared, to which there is added the anionic dispersing agent and/or the polymer or a polymer solution, the salt and, where

appropriate, further additives, and stirring is carried out until a homogeneous solution (or suspension) is obtained, and then all the water, with the exception of a residual amount, is removed from the aqueous solution in a drying step, solid particles (granules) simultaneously being formed.

36-39. (canceled)

40. (previously presented) A process according to claim 35, wherein the phthalocyanine solution is purified of organic by-products by a membrane separation procedure.

41. (previously presented) A granulate as defined in claim 1 with the proviso that it does not contain ethoxylated stearyldiphenyloxyethyldiethyltriamine.

42. (original) A granulate as defined in claim 41 with the proviso that it is not encapsulated and it has a substantially homogeneous distribution of ingredients.

43. (previously presented) A method of treating textiles which comprises contacting them with a formulation according to claim 1.